

THE ASSOCIATED MOLECULAR NATURE OF BITUMINOUS COAL

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INTRODUCTION

Coal is a complex mixture of organic material and inorganic components. Detailed characterization of the organic material is still impossible, even when using today's highly developed sophisticated analytical techniques. This is primarily due to the amorphous nature of high-molecular-mass mixtures. The understanding of the physical structure of these materials is an important step in the study of coal structure. The extent to which coal molecules may be (A) covalently cross-linked and/or (B) physically associated is illustrated in Figure 1.

A cross-linked, three-dimensional macromolecular model (Model A) has been widely accepted as a model of the organic material, with this framework occluding some solvent-extractable components. It is, however, this author's opinion that the evidence is indirect and there is little information to elucidate the real state of the physical structure of coal.

Intra- and intermolecular (secondary) interactions play an important role in Model B, but differentiation between covalent bonds and the strong secondary interactions has not been thoroughly studied. Our recent work (1-6) demonstrated the significance and importance of relatively strong secondary interactions in all ranks of coal. Therefore, the conventional coal structural Model A needs to be reinvestigated.

In this paper, our recent results will be summarized and investigated along with the relating past work. From this analysis, it is reasonable to deduce that significant portions (far more than generally believed) of coal molecules are physically associated.

EXPERIMENTAL

Most of the experimental procedures have been already reported in the previous papers (1-7). The followings are some of these outlines. American Chemical Society reagents and h.p.l.c.-grade solvents were used without purification. Coal samples were obtained from the Premium Sample Program at Argonne National Laboratory (8), the Pennsylvania State University Coal Bank and Exxon Research and Engineering Co.

Approximately 5 g of coal was placed in 100 ml of solvent in a 250 ml flask or a 300 ml autoclave and magnetically stirred under nitrogen. The mixture was either stirred at room temperature, heated, or mildly refluxed in an oil bath or in an autoclave heater. The cooled mixture was dried using a rotary evaporator, mixed with methanol, and filtered, while being rinsed with methanol several times. The coal was dried in a vacuum oven at 95°C overnight.

The experimental procedure of coal swelling is based on the earlier reported method (9,10). The measurements were performed in the disposable Wintrobe Tubes (Fisher Scientific) of 3 mm inner diameter and 115 mm in length with graduations in 1 mm divisions. After placing three weighed coal samples into the tubes, these tubes were centrifuged for 5 min (at 3600 rpm in a 30 cm diameter horizontal rotor). Bulk density of each coal under the condition was determined by the average height centrifuged. Each initial height before solvent swelling was calculated from weight of samples by using the bulk density. This is tedious compared to the conventional procedure but essential

to obtain reproducible results particularly at low coal concentration. Solvent was added to each weighed sample after measuring its volume, and the content was vigorously stirred with a thin rod. The tubes were centrifuged for 5 min at 3600 rpm. The volumetric swelling ratio (Q) was calculated by the difference between these heights of samples (9,10). Separate samples were employed for determining the extents of swelling as a function of time and coal concentration.

RESULTS AND DISCUSSION

Solvent extractability

There is a long history, over a century, of coal-solvent extraction. Only a small fraction of most coals is extractable in organic solvents. This amount may reach 20-30 wt%, and it has been thought that this limited solubility or extractability is consistent with Model A. Hydrogen bonds have been primarily considered in addition to relatively weak van der Waals' forces and they are assumed to be broken with one of the best solvents, pyridine (11,12). Caution, however, is advised against the limited extractability of coal, because it seems that the limited extractability originates from the disregard of various relatively strong secondary interactions caused by polyfunctional groups in coal.

The variety of relatively strong secondary interactions are present and their abundances are highly rank-dependent because of the dependence of the abundance of diverse functional groups on coal rank (1,4,6). It was estimated (1,4,6) that the Coulombic force is predominant in lower-rank coal due to ionized groups, that charge-transfer complexes involving non-ionizable but transferable electrons are important in medium-rank coal, and that dispersion forces involving polarizable π -electrons in polycyclic aromatics (π - π interactions) are major contributors in higher-rank coal.

Any single solvent does not appear to be able to disrupt all of these relatively strong secondary interactions and allow an efficient single step extraction. Macromolecules with relatively strong secondary interactions co-operatively interact (13). The co-operativity may make solubilization of coal more difficult. Therefore, another extraction procedure appropriate for coal needs to be explored.

A multistep sequence was proposed with the aim of minimizing various interactions step by step in the recent papers (6). Each step was selected to minimize the possibility of cleaving covalent bonds. Detailed mass balances and additional experiments to investigate the breaking of different secondary interactions were shown in the paper (6).

Each step to break or solvate relative strong secondary interactions has to be selected according to ranks of coals because of the rank dependence of the abundance of these interactions. The concept of this rank dependence may be represented as shown in Figure 2. For subbituminous coal, ionic forces and then charge-transfer interactions should be solvated step by step in addition to hydrogen bonds. For high-volatile bituminous coal, the solvation of π - π interactions would be important after breaking charge-transfer interactions.

The pyridine extraction yields for Argonne Premium coal samples by single step and multistep procedures were compared (6). Total extraction yields of 38-73 wt% (daf) were obtained by using multistep extractions except for low-volatile bituminous coal. These procedures are tedious but straightforward, and the extractabilities are much larger than those obtained by using the conventional extraction. Other results of high extractability using different methods has been available for selected ranks of coal (14-17).

Above results indicate that coal is extractable to a large extent if

various relatively strong secondary interactions are properly weakened. Therefore, limited extractability using a single step with an individual solvent may give a misleading information about coal structure. It is not logical to deduce any concept from the values.

Associative equilibria

If the relatively strong secondary interactions or physical associations are significant in coal, associative equilibria of coal should be observed in solvents. The associative equilibria, however, have not been fully appreciated for the system of coal and solvent regardless of such numerous observations for polymer solutions.

The solvent-induced association has been observed and interpreted as associative equilibria (1,2). Self-associations of high-volatile bituminous coal and its pyridine extract is induced by the solvent soaking. Heating or immersing these materials in poor solvents or in good solvents, followed by the removal of good solvents (the solvent treatment), caused decreases in their pyridine extractability. Any significant chemical reaction during the solvent treatment was experimentally ruled out.

Other associative equilibria were seen as changes in precipitation of extract solutions and molecular weight at different temperatures (3). It was observed that such associative equilibria are highly rank-dependent. This resulted in remarkable differences in extraction rate, effect of preheating on extraction and effect of solvent-soaking on extraction for A region (< ca. 87 % C), B region (ca. 87 to 90 % C) and C region (> ca. 90 % C) coals (3). This coincides with the significant rank dependence of types and abundances of relatively strong secondary interactions in coal considered for multistep extractions in the previous section.

From the above discussion, relatively strong secondary interactions exist in coal, and coal components (or molecules) equilibrate between association and dissociation due to these interactions even in good solvents such as pyridine. So, differentiation between chemical bonds and strong secondary interactions should be considered, although the quantitative assessment of their abundances is very difficult. Because of the presence of relatively strong secondary interactions, it is suggested that apparent networks experimentally observed, which have been often regarded as representing Model A, are much deviated from the phantom (real) networks, if any.

Solvent swelling

The behaviour of solvent(-induced) swelling without complete dissolution in any organic solvent has been often referred to the evidence for Model A. Sanada and Honda (18) applied the statistical theory of rubber elasticity to coal in order to estimate the average molecular weight between cross-links. Since then, solvent swelling has been used to characterize the macromolecular nature of coal by many workers (19,20). The author critiques this line of evidence for Model A on the grounds that coal swelling is not reversible and highly dependent upon coal concentration. Although a series of full papers will be reported elsewhere (21), some of recent results on these issues are shown.

1 Irreversibility of solvent swelling. Distinctively different physical phenomena have been observed in a solvent between the A and B region coals (3). Accordingly, pyridine swellings of Illinois no. 6 (IL: the A region) and Upper Freeport (UF: the B region coal) were compared. The swelling ratio Q at room temperature is very small as seen by UF-1 in Table 1, whereas the Q value at 70°C is larger and increased with time (UF-2). If the pyridine swelling is

mainly due to cross-linked covalent bonds in the coal, the significantly different Q between the two temperatures cannot be explained by elastic swelling. The result can be rationalized due to more disruption of secondary interactions at high temperature (70°C) (3).

The UF coal once swollen in pyridine, followed by the removal of pyridine, gave nearly the same Q value (UF-3) and pyridine extractability (3) as the raw coal. However, decreases in the Q value (IL-1 and 2 in Table 1) and extractability (3) were observed for the IL coal by the swelling/deswelling procedure.

Thermally induced dissociation which is significant for the B region coal was observed for UF-2 as shown above. However, if pyridine is removed from the B region coal after thermally induced dissociation by refluxing in pyridine, relatively strong association may occur as seen for the A region coal (3). The UF coal was refluxed in pyridine for 3 days, followed by the removal of pyridine, and then the swelling ratio Q of this sample was measured at room temperature (UF-4) and 70°C (UF-5). Both Q values at room temperature and 70°C of the sample were nearly equal to that of the raw coal. It is noted that an increase in the Q value was not observed at 70°C .

If pyridine solubles is removed from the coal after thermally induced dissociation, the coal may increase solvent swelling even when the coal was dried, because the solubles do not associate back with the residue. In fact, the swelling ratio Q of the pyridine extracted UF coal (PI) (UF-6) was larger than that of the raw coal. This is also notable, because PI of the IL coal (IL-3) showed the smaller Q value than the raw coal.

Therefore, solvent swelling is irreversible for the IL and the UF coals. The irreversibility is quite different between the IL and the UF coals. These distinctive differences are consistent with different physical phenomena between these ranks of coals discussed above.

2 Dependence of coal concentration on solvent swelling. The change in associative equilibria for residue may be detected by the dependence of coal concentration on solvent swelling. Therefore, swelling ratios of various coals and their PI were measured at various coal to solvent weight ratios (C/S) in room temperature pyridine.

The results for PSOC-1491 coal (high-volatile C bituminous coal) are summarized in this section. Swelling ratios of the raw coal and its PI versus C/S values are shown in Figure 3. In both cases, swelling ratios are highly dependent on coal concentration.

Most of Q by the volumetric method have been obtained at the large C/S value, and these Q can be regarded as the saturated value (Q_{∞}) (9,10). A gravimetric (18) and a piston type (22) of measurements are under the condition of the quite large C/S value without agitation. Therefore, these methods must also give the saturated swelling ratios. Because of the small dependence of concentration on solvent swelling at the larger C/S value, the conventionally obtained Q should be approximately reproducible regardless of C/S. However, caution should be exercised when coal structure is investigated by using these Q_{∞} , because the Q_{∞} are apparent values.

If soluble material during coal swelling significantly affect solvent activity and change solvent swelling, swelling of coal and residue must be significantly different against the C/S value. However, the results (Figure 3) show the approximately same dependence on sample concentration. The effect of solubles on solvent swelling was further examined. The PI from the PSOC-1491 coal was mixed with its PS, and their pyridine swelling ratios were measured at various mixing ratios at the C/S value of 0.2.

It was found that the swelling ratio Q of the mixture containing solubles

is simply determined by the additive of swelling of each fraction. As PS cannot completely dissolve in room temperature pyridine at the C/S value of 0.2, the undissolved PS behaves like residue and is swollen with pyridine. No significant effect of solubles in the solvent on the solvent activity was observed.

From these results, the dependence of coal concentration on solvent swelling indicates that secondary interactions are solvated more at lower concentration, associated coal dissociates more, and coal is swollen more.

A mono- or two-phase model?

It has been proposed that coal is composed of a macromolecular network (immobile phase) with relatively small molecules (mobile phase) occluded in the macromolecular network. This idea was recently described as the so-called two-phase model (23,24). The essence of this model states that only some portions (ca. 10-20%) of the mobile phase can be extracted using the regular extraction procedures because of restricted orifice sizes of the immobile phase. The two-phase model is readily compatible with Model A. However, there is no direct evidence to prove the two-phase model as reviewed in a recent paper (7). The problem is that no work has differentiated (a) between the extent of covalent bonds and physical associations, and (b) between the disruption of covalent bonds and physical dissociations.

The proposed two-phase model has been studied by two different approaches (7,25). Since major portions (70-90%) of high-volatile bituminous coal can be extracted with THF after heating (350°C) in *n*-butylamine (26), the physically trapped mobile phase should be released in the extract. The Illinois no. 6 coal extract from this treatment was further pyrolyzed, and typical mobile phase compounds were semi-quantitated in these samples (7). Although the detailed solvation mechanism in *n*-butylamine is not clear, the differences in amounts of such compounds between the original extract and further pyrolyzed samples are unequivocally due to degradation of chemical bonds. As the results showed, typical mobile phase molecules such as *n*-alkanes and polycyclic aromatic hydrocarbons were not released during the *n*-butylamine treatment, but were released by the thermal degradation of coal macromolecules. From this result, it was concluded that the two-phase model is not applicable for high-volatile Illinois bituminous coal. This work and another work (25) showed that *n*-alkanes, alkylbenzenes, alkylnaphthalenes, phenanthrene, and alkyl hydroaromatic pentacyclic triterpanes, which were regarded as the mobile phase, are important partial constituents of coal molecules regardless of molecular mass.

Consequently, coal can be regarded as a monophase rather than the two-phase model. The monophase model is more consistent with Model B rather than Model A.

CONCLUSION

On the basis of the preceding discussion, it can be suggested that the three major indications of Model A: (a) limited solvent extractability, (b) reversible solvent swelling and (c) the present concept of the two-phase model, are not entirely persuasive. It is reasonable to deduce from various results shown above that significant portions (far more than generally believed) of coal molecules are physically associated.

REFERENCES

- 1 Nishioka, M. and Larsen, J. W. Energy & Fuels 1990, 4, 100
- 2 Nishioka, M. and Larsen, J. W. Prepr. Am. Chem. Soc. Div. Fuel Chem. 1990, 35(2), 319
- 3 Nishioka, M. Energy & Fuels 1991, 5, 487
- 4 Nishioka, M., Gebhard, L. A. and Silbernagel, B. G. Fuel 1991, 70, 341
- 5 Nishioka, M. Energy & Fuels 1991, 5, 523
- 6 Nishioka, M. Fuel 1991, 70, 1413
- 7 Nishioka, M. and Gorbaty, M. L. Energy & Fuels 1990, 4, 70
- 8 Vorres, K. S. Energy & Fuels 1990, 4, 420
- 9 Green, T. K., Kovac, J. and Larsen J. W. Fuel 1984, 63, 935
- 10 Otake, Y. and Suuberg, E. M. Fuel 1989, 68, 1609
- 11 Larsen, J. W. and Baskar A. J. Energy & Fuels 1987, 1, 230
- 12 Painter, P. C., Sobkowiak, M. and Youtcheff, H. Fuel 1987, 66, 973
- 13 Tsuchida, E. and Abe, K. Adv. Polym. Sci. 1982, 45, 77
- 14 Iino, M., Takanoashi, T., Ohsuga, H. et al. Fuel 1988, 67, 1639
- 15 Mallya, N. and Stock, L. M. Fuel 1986, 65, 736
- 16 Miyake, M. and Stock, L. M. Energy & Fuels 1988, 2, 815
- 17 Chatterjee, L., Miyake, M. and Stock, L. M. Energy & Fuels 1990, 4, 242
- 18 Sanada, Y. and Honda, H. Fuel 1966, 45, 295
- 19 Larsen, J. W. and Kovac, J. in 'Organic Chemistry of Coal' (Ed. J. W. Larsen), American Chemical Society, Washington, DC, 1978, Ch. 2
- 20 Lucht, L. M. and Peppas, N. A. in 'New Approaches in Coal Chemistry' (Eds. B. D. Blaustein, B. C. Bochrath and F. Friedman), American Chemical Society, Washington, DC, 1981, Ch. 3
- 21 Nishioka, M. to be published
- 22 Aida, T and Squires, T. G. Am. Chem. Soc. Div. Fuel Chem. Prepr. 1985, 30(1), 95
- 23 Given, P. H. in 'Coal Science Vol. 3' (Eds. M. L. Gorbaty, J. W. Larsen and I. Wender), Academic Press, New York, 1984, pp. 63-252
- 24 Given, P. H., Marzec, A., Barton, W. A. et al. Fuel 1986, 65, 155
- 25 Nishioka, M. and Larsen, J. W. Energy & Fuels 1988, 2, 351
- 26 Tagaya, H., Sugai, J., Onuki, M. et al. Energy & Fuels 1987, 1, 397

Table 1 Swelling ratio (Q) in pyridine of UF and IL coals at room temperature (r.t.) and 70°C (21) (coal/solvent wt ratio: 0.20-0.25)

Code	Sample	Q							
		0	2h	4h	8h	16h	24h	48h	72h
UF-1	Raw coal (r.t.)	1.2	1.1	1.1			1.2	1.1	1.1
UF-2	Raw coal (70°C)	1.2	1.2	1.4	1.7	1.8	2.2		
UF-3	Coal swollen in pyridine followed by drying (r.t.)	1.0					1.0	1.1	1.1
IL-1	Raw coal (r.t.)	2.3	2.1	2.2	2.1	2.3	2.2	2.3	2.2
IL-2	Coal swollen in pyridine followed by drying (r.t.)	2.0	2.0	2.0	2.0		2.0	2.0	
UF-4	Coal refluxed in pyridine followed by drying (r.t.)	1.0					1.1	1.0	
UF-5	Coal refluxed in pyridine followed by drying (70°C)		1.0	1.1	1.0	1.1	1.1	1.1	
UF-6	Pyridine extracted coal (r.t.)	1.4					1.4	1.3	
IL-3	Pyridine extracted coal (r.t.)	2.0	2.0				2.1	2.0	

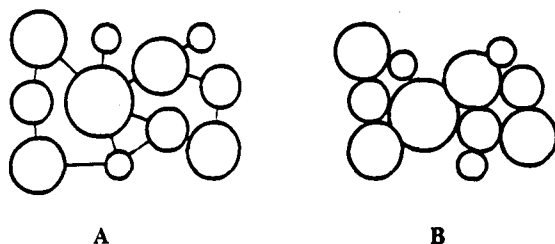


Figure 1 (A) Covalently cross-linked and (B) physically associated models of coal structure

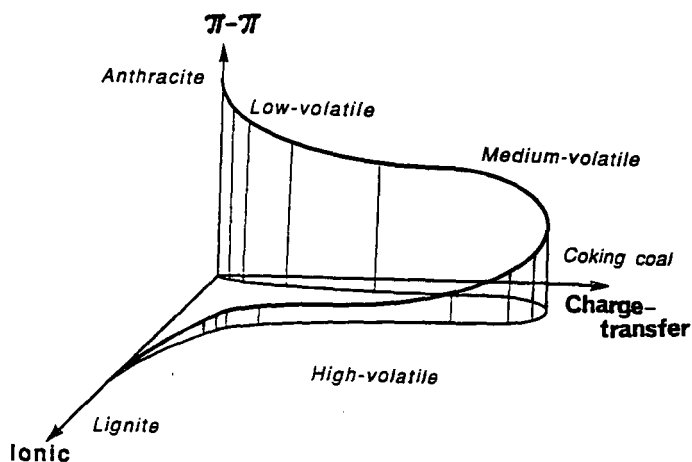


Figure 2 Proposed dependence of relatively strong intra- and intermolecular interactions on coal rank

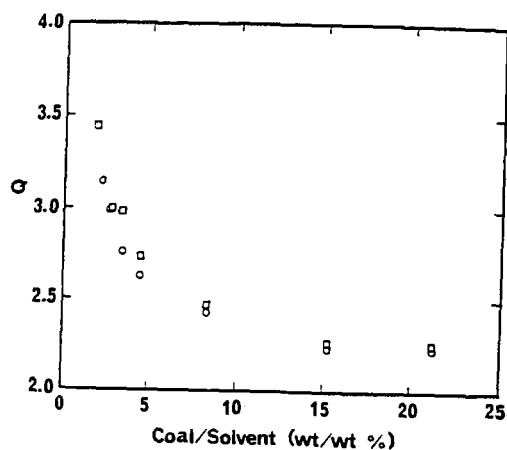


Figure 3 Swelling ratios (Q) in pyridine of PSOC-1491 native (\square) and its pyridine extracted (\circ) coals as a function of coal/solvent wt% (21)